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EP 929600 A1 E C08K-003/00 Based on patent WO 9814510

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JP 2001501251 W 11 C08L-077/00 Based on patent WO 9814510

Abstract (Basic): WO 9814510 A

A process for improving the colour stability of a polyamide resin comprises: (a) providing a moulding composition comprising: (i) 20-80 wt.% of a polyamide of melting point 280-340 deg. C; (ii) 0-50 wt.% of an inorganic filler; (iii) 10-35 wt.% of a flame retardant with 50-70 wt.% bromine; and (iv) 1-10 wt.% of an antimony compound; (b) adding 0.1-4 wt.% of zinc borate to the moulding composition; and (c) making a moulded part from the composition.

USE - For making moulded parts (claimed), e.g. a connector (claimed) used in surface mount technology.

ADVANTAGE - Adding the zinc borate allows the composition to be held for longer times in an extruder or moulding device with no decrease in the colour quality of the moulded part.

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Title Terms: COLOUR; STABILISED; FLAME; RETARD; POLYAMIDE; MOULD; RESIN; OBTAIN; ADD; ZINC; BORATE; ALLOW; LONG; TIME; EXTRUDE; TEMPERATURE; NO;

LOSS; MOULD; COLOUR; QUALITY

Derwent Class: A23; A85; E32; U11; V04

International Patent Class (Main): C08K-003/00; C08L-077/00

International Patent Class (Additional): C08K-003/22; C08K-003/38;

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C08L-077/00; C08L-077-00

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Manual Codes (EPI/S-X): U11-A07; U11-E02A1

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\*01\* A430 A940 B105 B701 B711 B720 B803 B831 C108 C802 C803 C804 C805

C807 M411 M781 M903 M904 Q010 Q120 Q621 R032 R03130-U

Polymer Indexing (PS):

<01>

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C08K 3/00, C08L 77/00, 25/18 // (C08K 3/00, 3:00, 3:38) (C08L 77/00, 77:00, 25:18) (C08L 25/18, 25:18, 77:00)</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/14510</b> <b>(43) International Publication Date:</b> 9 April 1998 (09.04.98)
<b>(21) International Application Number:</b> PCT/US97/16819 <b>(22) International Filing Date:</b> 22 September 1997 (22.09.97)  <b>(30) Priority Data:</b> 60/027,066 30 September 1996 (30.09.96) US  <b>(71) Applicant (for all designated States except US):</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> MIYABO, Atsushi [JP/JP]; Maison de Issey Takeda 507. 60-2, Takeda Jyobodai-in cho, Fushimi-ku, Kyoto 612 (JP). KOSHIDA, Reiko [JP/JP]; 2-14-19-608, Minowa, Kohoku, Yokohama 223 (JP).  <b>(74) Agent:</b> FORSTNER, James, A.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COLOR STABLE FLAME RETARDED POLYAMIDE RESIN  <b>(57) Abstract</b>  This invention relates to a process for improving the color stability of a polyamide resin by providing a molding composition comprising 20 to 80 weight percent of a polyamide having a melting point of from 280 °C to 340 °C; 0 to 50 weight percent of an inorganic filler; 10 to 35 weight percent of a flame retardant with 50-70 weight percent bromine, and 1 to 10 weight percent of an antimony compound, adding from 0.1 to 4 weight percent zinc borate to the molding composition. The above weight percents are based upon the total amount of polyamide, inorganic filler, flame retardant, antimony compound, and zinc borate only. Molding the molding composition to make a molded part is part of the invention.		

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TITLE

## COLOR STABLE FLAME RETARDED POLYAMIDE RESIN

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BACKGROUND OF THE INVENTION

Recent trends in surface mount technology (SMT) connectors require that the connectors have high heat stability and good flammability performance.

Among thermoplastic resins used for SMT connector applications, such as aromatic polyamides, 46 nylons, polyphenylene sulfide and liquid crystal polymers, a flame retardant should be used with the thermoplastic resin such that the resulting composition is V-0 according to the UL94 flammability test.

However, a problem with conventional compositions of a flame retardant and a thermoplastic resin is that when the compositions are extruded or molded, the compositions sometimes suffer a decrease in the quality of the color of the composition. For example, the composition may have a black streak or a brown substance that is believed to be due primarily to the decomposition of flame retardant.

ICI US Patent 4,105,621 discloses polyamide compositions containing glass fiber, halogenated flame retardant, zinc borate and a group of oxides including that of antimony. It does not recognize or suggest the problem of color stability upon molding.

BASF EP 410,301 discloses polyamide compositions containing brominated compounds, fillers, elastomer polymer and "synergistic metal oxide and/or metal borate." Again, color stability is not suggested.

SUMMARY OF THE INVENTION

This invention relates a process for improving the color stability of a polyamide resin providing a molding composition comprising 20 to 80 weight percent of a polyamide having a melting point of from 280°C to 340°C; 0 to 50 weight percent of an inorganic filler; 10 to 35 weight percent of a flame retardant with 50-70 weight percent bromine; and 1 to 10 weight percent of an antimony compound; adding from 0.1 to 4 weight percent zinc borate to the molding composition; where the above weight percents are based upon the total amount of polyamide, inorganic filler, flame retardant, antimony compound, and zinc borate only; and molding the molding composition to make a molded part.

DETAILED DESCRIPTION

The present invention allows an expansion of the use of halogen type flame retardants in polyamides using antimony oxides with a longer resin hold up  
5 times in an extruder or molding device while obtaining an improved color quality.

This invention relates a process for improving the color stability of a polyamide resin by providing a molding composition comprising 20 to 80 weight percent of a polyamide having a melting point of from 280°C to 340°C; 0 to 50 weight percent of an inorganic filler; 10 to 35 weight percent of a flame  
10 retardant with 50-70 weight percent bromine; and 1 to 10 weight percent of an antimony compound; adding from 0.1 to 4 weight percent zinc borate to the molding composition, wherein the above weight percents are based upon the total amount of polyamide, inorganic filler, flame retardant, antimony compound, and zinc borate only; and molding the molding composition to make a molded part.

15 This invention also relates to molded parts and connectors made from this process.

The polyamide used in this invention may be any polyamide that has a melting point of from about 280°C to about 340°C. An example of a suitable polyamide is a copolyamide composed of 20-80 mole % of units derived from hexamethylene terephthalamide and 80-20 mole % of units derived from  
20 hexamethylene adipamide. This polyamide is referred to hereinafter as 6T/66 copolymer. Other suitable polyamides include polyamides composed of 20-80 mole % of units derived from hexamethylene terephthalamide and 80-20 mole % of units derived from hexamethylene sebacamide, hexamethylene dodecamide, hexamethylene isophthalamide, 2-methylpentamethylene terephthalamide, or  
25 mixtures thereof.

There are no particular limitations on the process for the production of the copolyamide used in the composition of the present invention. It may be produced easily by ordinary melt polymerization. One method to produce the copolymer of this invention is an autoclave one-step polymerization process  
30 taught in US Patent No. 5,378,800. That process includes feeding to a reactor an aqueous salt solution of an admixture of desired diacids and diamines, heating the solution under pressure, reducing the pressure, maintaining the reaction mixture at a pressure that is not greater than about atmospheric pressure, and discharging the polyamide from the reactor. An alternative process includes preparing a  
35 prepolymer and subjecting the prepolymer to solid-phase polymerization or melt-mixing in an extruder to increase the degree of polymerization. The prepolymer is prepared by heating at 150°C-320°C an aqueous solution containing 6T salt (a salt formed from hexamethylenediamine and terephthalic acid) and 66 salt (a salt

formed from hexamethylenediamine and adipic acid). An alternative process consists of subjecting 6T salt and 66 salt directly to solid-phase polymerization at a temperature lower than the melting point.

5 The composition of the present invention contains an inorganic filler or reinforcing agent that includes, for example, fibrous reinforcement such as glass fiber and carbon fiber, glass beads, talc, kaolin, wollastonite and mica. Preferable among them is glass fiber. Glass fibers suitable for use in the present invention are those generally used as a reinforcing agent for thermoplastics resins and thermosetting resins. Preferred glass fiber is in the form of glass rovings,  
10 glass chopped strands, and glass yarn made of continuous glass filaments 3-20 micron meters in diameter.

The resin composition of the present invention contains a flame retardant. It is a flame retardant based on brominated polystyrene and/or brominated poly-phenylene ether containing 50-70% by weight bromine. The  
15 polystyrene has a weight-average molecular weight higher than 5000, preferably higher than 20,000, and more preferably higher than 28,000. The ether has a molecular weight of at least 6000. A preferred flame retardant is brominated polystyrene or polydibromostyrene.

In a composition according to the present invention, the  
20 bromine-containing flame retardant is used in combination with an auxiliary flame retardant that is a specific antimony compound which is selected from the group consisting of antimony trioxide, antimony tetraoxide, antimony pentoxide and sodium antimonate. Sodium antimonate is preferred.

It is possible to attain a UL-94 (test date October 29, 1996) rating of  
25 V-0 using the compositions described above without zinc borate. However, the polyamides of this invention have inherently high processing temperatures because of the relatively high melting point of the polyamides of 280°C to 340°C. These high processing temperatures can cause a black streak or discoloration of the polymer during extrusion and molding.

30 Therefore an important feature of this invention is the addition of zinc borate to the compositions described above. Zinc borate is known in the art as being effective as a drip suppressant, a flame retardant synergist for improving the tracking performance of a resin, and for improving corrosion resistance. However, the present invention is based on the discovery that when zinc borate is  
35 added to the composition of a polyamide, an inorganic filler, a flame retardant and an antimony compound as described above, the resulting molding composition exhibits improved color when molded. Further, the molding composition may be

held under longer hold times in a molding device with no decrease in the color quality of the molded part.

The copolyamide resin of the present invention may have incorporated in it a variety of additives such as an impact modifier, a viscosity modifier, pigment, dye, antioxidant, and heat resistance improver, in such amounts that they do not harm its characteristic properties.

### EXAMPLES

The present invention is illustrated by the following examples and comparative examples.

A mixture of 6T/66 (55/45 mole percent), sodium antimonate sold as Sunepoch® NA1070L by Nissan Chemical, PDBS-80™ polydibromostyrene (contains 59 weight percent bromine) sold by Great Lakes, and Firebrake® 290 zinc borate ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ) or Firebrake® 500 zinc borate ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3$ ) sold by Borax, was extruded on twin screw extruder equipped with a side feeder (ZSK-40, W&P) and pelletized. In Examples 4 and 6, the flame retardant was Pyro-Chek® 68PBC brominated polystyrene supplied by Ferro (contains 66 weight percent bromine).

All the samples contained 1.0% of DuPont's Surlyn® 8920 (sodium ionomer resin) and 0.2% Hoechst PED 521 (oxidized polyethylene wax). The remainder of each composition was polyamide.

The color stability of the pelletized mixture was evaluated by molding at 340°C a plate having dimensions of 50 mm by 90 mm by 3.2 mm while varying the hold up-time in the mold among 3 minutes, 10 minutes and 15 minutes. Conventional molding processes typically use a hold-up time of less than 10 minutes. All the mechanical properties were measured using ASTM test procedures:

Tensile Strength and Elongation:	ASTM D638-95
Flexural Modulus and Strength:	ASTM D790-95A
Notched Izod Strength:	ASTM D256-93A

All were in the ASTM volume dated June 1996.

Flammability was tested according to UL94 using molded bars with a 1/32 inch thickness (0.79375 millimeters).

The results from the Examples are summarized in the Table below. Examples 1 to 4 show that zinc borate improved the color stability of the polyamide resin composition.

In Examples 1 to 3, the composition that included polydibromostyrene flame retardant exhibited color stability even after a 15-minute hold time. In Example 4, the composition that included the Pyrochek® flame retardant, also showed color stability. The molded part had a color lighter than the molded part in Example 6. The mechanical properties showed no deterioration even when 2% of zinc borate was added. In Examples 1-4, stability was good even after 10 minutes at 340°C.

Examples 5-7 are comparative Examples. Comparative Example 5 showed a lack of color stability because it exhibited a black streak on the molded part after a 10-minute hold time. In Comparative Example 7, there was an improvement in color stability of the molded part after the addition of 0.06% of zinc borate, but the improvement was not significant.



TABLE

No.		Examples							Comparative Examples		
		1	2	3	4	5	6	7			
Base Nylon Type		6T/66	6T/66	6T/66	6T/66	6T/66	6T/66	6T/66	6T/66	6T/66	6T/66
Glass	(%)	30	30	30	40	30	40	30	40	30	30
PDBS-80™	(%)	24	24	24	-	24	-	24	-	24	24
Pyro-check® 68PBC	(%)	-	-	-	17	-	17	-	17	-	-
Sodium Antimonate	(%)	4	4	4	2	4	4	4	4	4	4
Firebrake® 290	(%)	0.15	0.3	0.9	-	0	0	0	0	0.06	0.06
Firebrake® 500	(%)	-	-	-	2	-	-	-	-	-	-
Tensile Strength	(MPa)	151	161	150	208	203	150	150	203	150	150
Elongation	(%)	1.8	2.0	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Flex Strength	(MPa)	212	230	207	282	274	213	213	274	213	213
Flex Modulus	(MPa)	10272	10407	10379	14621	150	14676	10300	14676	10300	10300
Notched Izod	(J/m)	71	84	64	116	1.8	110	69	110	69	69
Flammability (1/32"t)	UL94	V-0	V-0	V-0	V-0	209	V-0	V-0	V-0	V-0	V-0
State after 3 min at 340°C		A	A	A	A*	A	A	A	A	A	A
State after 10 min at 340°C		A	A	A	-	C	-	B	-	B	B
State after 15 min at 340°C		C	B	A	-	D	-	C	-	C	C

A: No black streak on sprue, runner and molded parts C: Black streak on sprue, runner and edge of molded parts

B: Black streak only on sprue and runner D: Black streak on sprue, runner and more than half area of molded parts.

\* = lighter color than Example 6

**WHAT IS CLAIMED IS:**

1. A process for improving the color stability of a polyamide resin, comprising the steps of:

5 providing a molding composition comprising 20 to 80 weight percent of a polyamide having a melting point of from 280°C to 340°C; 0 to 50 weight percent of an inorganic filler; 10 to 35 weight percent of a flame retardant with 50-70 weight percent bromine; and 1 to 10 weight percent of an antimony compound.

10 adding from 0.1 to 4 weight percent zinc borate to the molding composition,

where the above weight percents are based upon the total amount of polyamide, inorganic filler, flame retardant, antimony compound, and zinc borate only; and molding the molding composition to make a molded part.

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2. A molded part made from the process of claim 1.

3. A connector made from the process of claim 1.

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/16819

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K3/00 C08L77/00 C08L25/18 //(C08K3/00,3:00,3:38),  
(C08L77/00,77:00,25:18),(C08L25/18,25:18,77:00)

According to International Patent Classification(IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 410 301 A (BASF AG) 30 January 1991 cited in the application see page 9 - page 10 see claims 1-10 ---	1,2
X	US 4 105 621 A (MASLEN JOHN ET AL) 8 August 1978 cited in the application see claim 1 ---	1,2
X	DATABASE WPI Section Ch, Week 9431 Derwent Publications Ltd., London, GB; Class A23, AN 94-253002 XP002049839 & JP 06 184 431 A (ASAHI KASEI KOGYO KK) , 5 July 1994 see abstract --- -/--	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search

11 December 1997

Date of mailing of the international search report

02/01/1998

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Int. Application No  
PCT/US 97/16819

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI  Section Ch, Week 9431  Derwent Publications Ltd., London, GB;  Class A13, AN 94-253001  XP002049840  &amp; JP 06 184 430 A (ASAHI KASEI KOGYO KK) ,  5 July 1994  see abstract</p> <p>-----</p>	1-3

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/16819

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0410301 A	30-01-91	DE 3924869 A CA 2019904 A DE 59007375 D ES 2060874 T JP 3066755 A	31-01-91 27-01-91 10-11-94 01-12-94 22-03-91
US 4105621 A	08-08-78	GB 1572497 A AT 356898 B AU 507925 B AU 2192877 A BE 851665 A CA 1090031 A CH 626904 A DE 2706827 A FR 2341619 A JP 1397633 C JP 52102364 A JP 61058496 B NL 7701565 A, B, SE 432108 B SE 7701605 A ZA 7700487 A	30-07-80 27-05-80 06-02-80 10-08-78 22-08-77 18-11-80 15-12-81 01-09-77 16-09-77 07-09-87 27-08-77 11-12-86 23-08-77 19-03-84 21-08-77 28-12-77